Uranium levels in the Naryn and Mailuu-Suu rivers of Kyrgyz Republic

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As part of an international collaboration (the Navruz Project) between Kazakhstan, Kyrgyzstan, Tajikistan, Uzbekistan, and the United States of America on transboundary river monitoring, the Radiometric Laboratory of the Institute of Physics in Kyrgyzstan measured the isotopic composition of uranium (as measured by γ, the ratio of activities of $^{234}U/^{238}U$) for the water of the Naryn River basin. This ratio varies from 1.5 to 1.9 due to natural causes. The results point to the lack of the technogenic uranium along the Naryn River through territory of the Kyrgyz Republic and to the contamination of the Mailuu-Suu River by technogenic uranium from tailing dumps in the area. The share of technogenic uranium transported to Uzbekistan does not exceed 30%, and the total uranium content is considerably lower than the maximum admissible concentration (MAC) and is almost an order of magnitude lower than that of potable waters of the Chui Valley of Kyrgyz Republic.

Introduction

Mining and processing of radioactive and other raw materials in the Kyrgyz Republic has resulted in a series of waste deposits and dumps. Furthermore, continued operation of these enterprises can also negatively impact the environment not only in Kyrgyzstan, but also in adjacent states, such as Uzbekistan and Kazakhstan. Toxic chemicals can enter territories of adjacent states via the large Kyrgyz rivers, the Naryn and Mailuu-Suu, tributaries of the Syrdarya, which originate in Kyrgyzstan. The Syrdarya crosses into Uzbekistan, and flows through Kazakhstan to terminate in the Aral Sea. Migration of toxic contaminants has not been sufficiently studied, so radiation and other ecological hazards, as a rule, cannot be forecast.

Possible sources of water contamination in basin of the Syrdarya are as follows:

Gold-processing plant at Kumtor

The Kumtor mine was built in accordance with the General Agreement on the Design Kumtor and resolutions of the Government of Kyrgyz Republic on May 31, 1994 (No. 379), and on December 28, 1994 (No. 895). Local working designs were submitted for expert review to the Ministry of Environmental Protection of the Kyrgyz Republic.

The most severe environment effects involve the mine's waste facilities. Several of the waste-handling features are:

Pulp-line with an armature installed on it and stations for reducing pressure;
Emergency ponds for gathering leakage from the pulp-line;
Waste deposit dam with crest at 3652 m elevation (3649 m before it was raised in 2000);
Drain canal to the Arabel River (the upper drain canal);
Mountain ditch (the lower drain canal);
Refining buildings for purification of effluents from waste deposits.

As of September 30, 2000, the volume of the waste deposits was 16.9 million m^3, with liquid waste totaling 4.62 million m^3 and covering 2.15 million m^2. Financial constraints have prevented installing all planned safety measures at the plant. Therefore, waste materials from the deposits may be introduced into the Kumtor River, one of the tributaries of the Naryn River.

Coal deposit at Tashkumyr

The Tashkumyr coal deposit is located in the south of the Kyrgyz Republic at Tashkumyr on the Naryn River. The deposit has been exploited since 1916. Tashkumyr coal is of high quality; its ash content does not exceed 20%, moisture content is 6%, sulfur is 2%, and heat of combustion is 5000–5500 kcal/kg. A distinctive feature of Kyrgyz coal is a high radionuclide content, which can contaminate the environment when the coal is burned. This was confirmed at the implementation of the International Science and Technology Center (ISTC) Project KR-072-97, where it was shown that the ash from the thermal power station at the Karabalty Mining Combine (KMC) contains more toxic components than do the plant's solid wastes.

West Mining Chemical Combine at the town of Mailuu-Suu

In the area of the Mailuu-Suu River (tributary of the Karadaria, which flows into the Syrdarya) are waste deposits and dumps from the West Mining Chemical Combine (deposits 13 and 15). They contain about

4 million tons (2 million m^3) of highly toxic wastes, including uranium, decay products (thorium, radium, etc.), and radon emanations, roughly equivalent to $6 \cdot 10^4$ Bq. In addition to local wastes, radioactive wastes were imported from Germany that also contained arsenic (deposit 3). Deposits 5, 6, and 7, are subject to flood hazards. Often, mud flows (landslides), high seismic activity, and runoff can allow infiltration of highly toxic wastes into the waters of the Mailuu-Suu River. There is also a risk that the dams restraining the hazardous wastes might be breached.

Experimental

Determining the ratio of activities (γ) and uranium content (C_U) comprises the following steps.

Field water sampling and uranium concentration

The α-spectrometric method is the easiest and least expensive for determining isotopic composition and uranium concentration in natural waters. For accuracy in the measurement, it is necessary to have about 10^{-5} g of radiochemically pure uranium. That is, if the sampled waters have uranium content $C_U = 10^{-6}–10^{-7}$ g/l, samples should be extracted from a volume of 10–20 l.[1]

Field methods of uranium concentration from waters involve deposition on sorbents such as charcoal, ferric hydroxides, aluminum, titanium, or ion-exchange gums.[2,3,5] Powdered birch charcoal has a good reputation as a sorbent for uranium in cold water with minimal mineralization, adsorbing not less than 80% of the uranium in the water.

To simultaneously determine the uranium content and its isotopic composition (and control the loss of uranium from the water after sampling), a tracer may be added. This is an artificial, long-lived isotope of uranium in which the α-radiation energy noticeably differs from the energy from natural isotopes such as ^{234}U, ^{235}U, ^{238}U (4.2–4.8 MeV). The isotope ^{232}U most fully meets these conditions, with a half-life of 74 years and α-radiation energy of 5.3 MeV. The amount of tracer should be chosen so that its activity is commensurate (equal or less) with activity of natural uranium isotopes in the analyzed water.

Concentration of uranium is measured in the field using the following procedure. If the natural water is turbid, it is necessary to filter it or let the samples settle to remove suspended particles. Then the samples are decanted, using hoses, into graduated glass or polyethylene containers. To this water, hydrochloric acid, sulfuric acid, or nitric acid is added in the amount of 1 ml for 20 l of solution to bring the pH to 1–2. Methyl orange indicator is added, and the mixture is stirred with a special mixer or blowers. The odor of hydrogen sulfide can be eliminated with a blower. After

this, any excess acid is neutralized by 20% urotropine buffer to bring the pH up to 4.5–5.5. At this pH, the indicator's pink color changes to a light yellow.

To every 10 l of water 3–5 g of powdered charcoal is added and carefully stirred for 7 minutes. Then the water is left unstirred until the charcoal is deposited on the bottom of the container. After precipitation, the water is removed through a rubber tube, and the charcoal, along with some residual water, is filtered with a "white ribbon" filter with the help of a funnel for vacuum aspiration. The charcoal on the filter is washed two or three times with distilled water and air-dried, packed in filter paper, placed into a marked envelope, and transported to laboratory for further chemical processing.

Radiochemical clearing of uranium and preparing of preparations for physical measuring

Desorption of the uranium from the charcoal, radiochemical clearing from the coprecipitated elements, and preparation for α-spectrometric measurements is carried out under laboratory conditions. Charcoal is filtered into 250-ml glasses, topped up with 150 ml of hot 5% soda solution or 10% carbonic ammonium solution, stirred, and, after several hours, filtered by funnel for vacuum aspiration with a white ribbon filter. It is then washed with distilled water and thrown. The filtrate with the uranium desorbed from the charcoal is neutralized with hydrochloric or nitric acid and boiled for 30–40 minutes to remove the carbonic acid. Two or three drops of perhydrolum for organic materials disintegration may be added several times. Then, two or three drops of 1% ferric chloride solution cleared of radionuclides are added. The iron is precipitated by ammonia without charcoal as hydroxides and co-precipitated uranium. The precipitated ferric hydroxides together with uranium are dissolved into hot 1 mol/l nitric acid. To the nitrate solution sufficient ammonium nitrate is added to double the solution. After complete dissolution of the ammonium nitrate, the uranium is extracted by ethoxy ethane. Ethoxy ethane is added in an amount equal to the extracted solution. Uranium is extracted triply for 5 minutes. The ethereous extracts are boiled out in a water bath. The residual is decomposed by a mixture of 3% concentrated nitric acid and dissolved in 80 ml of distilled water. Then 1 ml of 10% solution of soda is added, and the solution is boiled for 5 minutes.

The solution is added to a dismountable teflon electrolysis container with a capacity of 100 ml. The container is composed of a cylinder screwed into a teflon base on the bottom of which there is a polished disk of stainless steel. The disk is 40 mm in diameter, and 1 mm thick. The disk acts as the cathode, and a platinum cone is used as the anode. Optimal conditions

for electrolysis are 0.5% Na_2CO_3 solution, current density 10–20 mA/cm^2, electrolyte temperature 80–90 °C, electrode separation 15–20 mm, and duration of electrolysis 1 hour.

After electrolysis, the disk is washed with distilled water and heated to red hot. The quality of the targets thus obtained meets the requirements for α-spectrometric measurements. The radionuclide is spread uniformly over the entire area of the disk and the radionuclide coating is strongly adhered to the disk and its density does not exceed 20-mkg/cm^2.

Nuclear-physical measurements of isotopic composition and concentration of uranium in samples

Isotopic composition of natural uranium is most effectively studied by α-spectrometry.[5,6] Current α-spectrometers use semiconductor detectors (SCD) and have a high power resolution.[7] However, for measuring activity of long-lived nuclides, their application is limited because the thickness of analyzed preparations cannot exceed 50–100 μg/cm^2. For isotopes of uranium, under the indicated conditions, the specific activity of preparations is less than 1 decay cm^{-1}·s^{-1}, so large source areas are required. In this case, it is expedient to utilize impulsive ionization chambers, which allow measurement of a much greater area. For these measurements, the ionization α-spectrometers, developed in the Radiometric Laboratory of IPh NASc KR were used.[6]

Results and discussion

This section presents the results of determining the C_U and the ratio of activities ($^{234}U/^{238}U$) in waters of the Naryn and Mailuu-Suu Rivers and leaching from mountain rocks at the sampling locations. Sampling locations are shown in Fig. l. Sampling was carried out under the auspices of the Navruz Project, an international collaborative program of transboundary monitoring of the rivers between the Republics of Kazakhstan, Kyrgyzstan, Tajikistan, and Uzbekistan. The United States was also a participant. Detailed information can be obtained on a web site.[14]

In each indicated location, as much as 20 l of water were sampled. Samples were prepared for measurement as described. Samples of the rocks were exposed to consequent water leaching during one week (first leach) and one month (second leach). The results are shown in Table 1. The preliminary conclusions on leaching (without the data included here) are given in an earlier work.[8] With allowance for the data on leaching, the results are as follows.

The Chong-Naryn and Kichi-Naryn rivers merge to form the Naryn River. Isotopic parameters of these river waters are similar; γ for the two rivers are equal within inaccuracies of measurement, and uranium content differs less than 40%. Isotopic composition in Sample 3 (the Naryn River above the town of Naryn) is higher than that in the Chong-Naryn and Kichi-Naryn, and uranium content is lower. There are no uranium processing plants there, and the change might be explained by dilution of the Naryn River water by the Orto-Kura, Bash-Kura, and other tributaries, in which the uranium content is possibly lower and the γ higher. This explanation, however, is not completely convincing, because the radionuclide content of the river discharge is considerably more than that of the tributaries. That disagrees with earlier opinion about sustainability of γ along a riverbed flow.[4,5,9] Additional sampling in the left tributary (Sample 2a) also confirmed that isotopic composition is suggestive of leaching and washing of rocks by waters of the Chong-Naryn and Kichi-Naryn Rivers. Therefore, changing of isotopic parameters of the waters can be explained by phase interchanging processes of uranium. Further, before the Naryn River leaves the borders of the Republic, isotopic parameters change a little. This points to the end of the process of forming γ, and indicates the feasibility of conducting balance studies of non-equilibrium uranium on that site.[10] Uranium isotopic composition in the first leaches for these samples varies from 1.0 to 1.3, but no variation of isotopic composition of the Naryn River water is noticeable. Isotopic composition for the second leaches is higher than 15–20%, but does not reach these values for the river waters. That points to absence of uranium phase interchange on this site. Figure 2 shows the variation of the content of uranium (10 g/l) with a blue line and γ with a red line. The figure shows that with increased γ, uranium content decreases. This confirms a mechanism that forms a surplus of ^{234}U and points to an absence of contamination by technogenic uranium of the Naryn River in Kyrgyzstan.

The results of determining γ and uranium concentration in the basin of the Mailuu-Suu River (Samples 11–15) (Table 1 and Fig. 3) are of great interest.

In the Sere-Suu River, a tributary of the Mailuu-Suu, the uranium concentration is $0.37 \cdot 10^{-6}$ g/l. In the Mailuu-Suu River before confluence with the Sere-Suu, the uranium concentration is $1.2 \cdot 10^{-6}$ g/l, then it increases to $3.1 \cdot 10^{-6}$ g/l (in the town of Mailuu-Suu). Farther down-river, the uranium concentration drops, and at the border with Uzbekistan, it is $1.8 \cdot 10^{-6}$ g/l. Accordingly, the ratio of activities γ changes from 1.39 (upstream) to 1.05 (in town), and 1.32 on the boundary with Uzbekistan. These circumstances point first to enrichment of the river waters by technogenic uranium, approximately 70% (γ=l), and the further sorption of this uranium (~60%) by riverbed rocks.

Table 1. Ratio of activities and uranium concentration in waters of the Naryn and Mailuu-Suu rivers and in leaches of the rocks in sampling locations

| Sample No.	Location	$^{234}U/^{238}U = \gamma$	C_U* 10^{-6} g/l	1-st leach		2-nd leach	
				$^{234}U/^{238}U = \gamma$	C_U* mg/kg	$^{234}U/^{238}U = \gamma$	C_U* mg/kg
1	The Chong-Naryn river	1.53 ± 0.05	0.90	1.42 ± 0.08	0.045	1.22 ± 0.01	0.017
2	The Kichi-Naryn river	1.52 ± 0.05	1.24	2.04 ± 0.05	0.056	1.11 ± 0.05	0.016
2a	Left tributary of the Naryn after confluence of the Chong-Naryn with Kichi-Naryn	1.29 ± 0.05	0.36	–	–	–	–
3	The river Naryn before town Naryn	1.86 ± 0.05	0.54	1.28 ± 0.05	0.039	1.22 ± 0.08	0.032
4	The At-Bashi river before falling into the Naryn	1.69 ± 0.05	0.85	1.04 ± 0.05	0.052	1.39 ± 0.07	0.025
5	The Naryn river after confluence with the At-Bashi river	1.61 ± 0.05	0.85	0.99 ± 0.03	0.068	1.28 ± 0.08	0.032
6	The Naryn river before Toktogul reservoir	1.70 ± 0.02	1.9	1.04 ± 0.04	0.056	1.30 ± 0.09	0.014
7	The Chichkan river before falling into Toktogul reservoir	1.27 ± 0.03	1.29	0.97 ± 0.04	0.045	1.40 ± 0.09	0.014
8	Toktogul reservoir	1.86 ± 0.02	1.0	1.13 ± 0.03	0.057	1.14 ± 0.06	0.041
9	The Naryn river after Toktogul reservoir	1.77 ± 0.02	1.0	1.04 ± 0.03	0.051	1.12 ± 0.09	0.031
10	The Naryn river on boundary with Uzbekistan	1.88 ± 0.02	0.9	1.25 ± 0.08	0.022	1.21 ± 0.14	–
11	The Sere-Suu river	1.39 ± 0.07	0.37	–	–	–	–
12	The Mailuu-Suu river	1.31 ± 0.04	1.2	–	–	–	–
13	The Mailuu-Suu river in Mailuu-Suu town near Transformer plant	1.05 ± 0.02	3.1	0.99 ± 0.03	0.013	1.44 ± 0.12	0.017
14	The Mailuu-Suu river after Mailuu-Suu town	1.06 ± 0.04	2.1	0.97 ± 0.04	0.076	1.35 ± 0.10	0.024
15	The Mailuu-Suu river on boundary with Uzbekistan	1.32 ± 0.02	1.8	1.03 ± 0.02	0.074	1.26 ± 0.07	0.030

* Error of uranium concentration is approximately 5%.
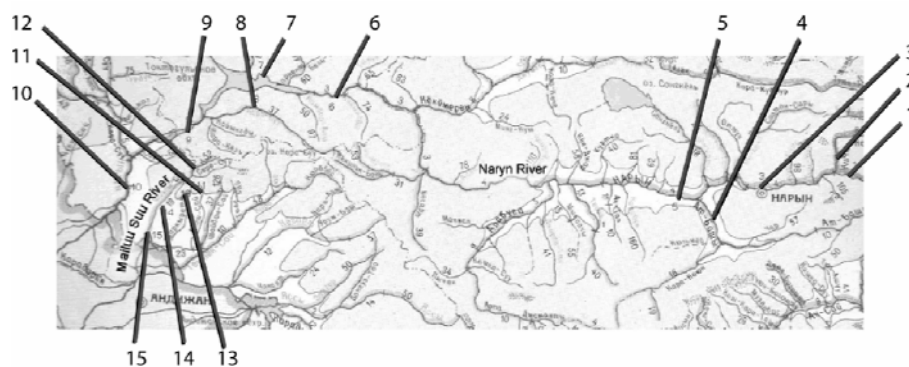
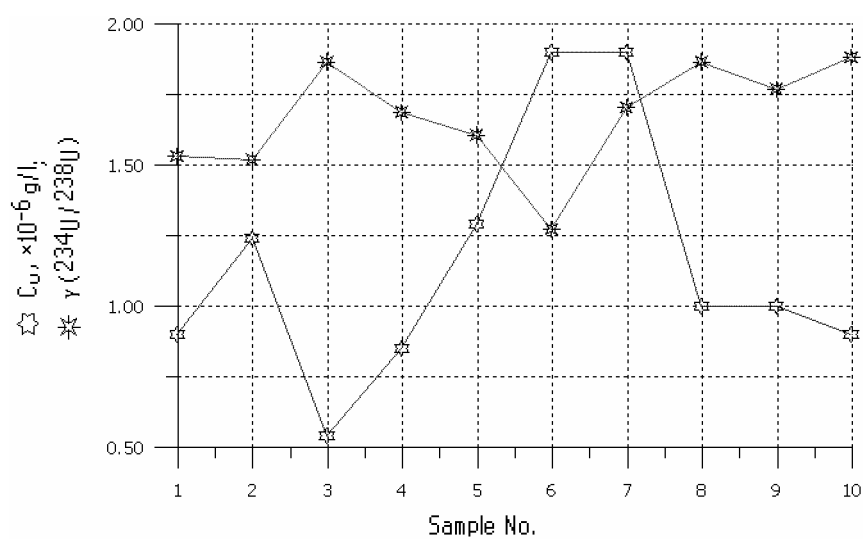*Fig. 1.* Locations of sampling in the Naryn and Mailuu-Suu river basins

Fig. 2. Ratio of activities (γ) and uranium concentration (C_U) in the Naryn River basin
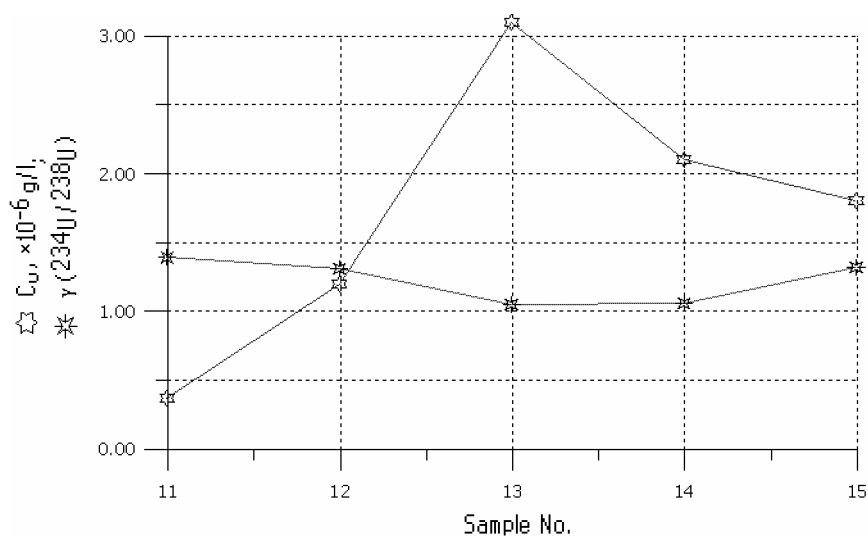

Fig. 3. Ratio of activities (γ) and uranium concentration (C_U) in the Mailuu-Suu river

Note that the uranium concentration in potable water of the Chui Valley in Kyrgyz Republic, according to the data of CHALOV, TUZOVA, and ALEKHINA,[11] varies from $4 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ g/l and more. That is an order of magnitude higher than in the Mailuu-Suu River. Detailed study of ecological hazards of waste deposits at WMChC in Kyrgyzstan was carried out by a group of specialists headed by I. T. AITMATOV, the director of Institute of Physics and Mechanics of Mountain Rocks (IPhMMR) of NASc KR. According to their data, the background uranium concentration in water is $3 \cdot 10^{-6}$ g/l,[12] which corresponds to a maximum value obtained by the authors during the Navruz project. However, as noted by NARMETOV and GOLDSTEIN,[13] the uranium concentration in the Mailuu-Suu River in Uzbekistan (more than 30 km down the river from WMChC) averages $1.9 \cdot 10^{-5}$ g/l, or one order of magnitude higher than the maximum value we observed (i.e., the same values as Chu Valley water).[11] This excess is apparently uranium from the Mailuu-Suu waste deposits. In this connection, AITMATOV, TORGOEV, and ALESHIN[12] recommend reburying the wastes in safer locations such as abandoned underground mines located next to the waste deposits and dumps using the experience of remediation of similar wastes in the United States and Germany. However, after taking into account all the results of studies of the WMChC to date, the practicality of reburying the wastes is doubtful. The reason for the excess of uranium and other toxic materials in Uzbekistan cannot be uniquely connected with the activity of WMChC. The question is whether this excess is of technogenic or natural origin and whether Kyrgyzstan is the source of radioactive contamination in Uzbekistan. Without additional study, it is impossible to answer these questions definitively.

Data on uranium leaching from rocks and washing by the waters of the Mailuu-Suu River confirm contamination of waters by technogenic uranium and sorption of this uranium by rocks. Therefore, the isotopic composition ratio for the first leaches is $\gamma=1$ ($\gamma=1.0$ for technogenic uranium), and for the second leaches, it is close to isotopic composition of the river's headwaters. That means that leaching during the first week desorbs practically all technogenic uranium, and then the natural uranium is desorbed. These data point to a higher mobility of technogenic uranium.

Conclusions

In all sampling locations, the uranium content does not exceed $3 \cdot 10^{-6}$ g/l. It is significantly lower than the maximum allowable concentration (MAC), or one order of magnitude lower than in potable water of the Chu Valley.

Isotopic composition (ratio of activities $^{234}U/^{238}U = \gamma$) in the Naryn River varies from 1.25 to 1.8, which points to different origins of the river water.

In upper stream of the Mailuu-Suu River, the uranium concentration is $0.37 \cdot 10^{-6}$ g/l. In the town of Mailuu-Suu (after waste deposit) it is $3.1 \cdot 10^{-6}$ g/l, almost one order of magnitude higher than on the boundary with Uzbekistan – $1.8 \cdot 10^{-6}$ g/l, or 1.7 times lower than in the town. Accordingly, changes in ratios of activities from 1.39 (upstream) to 1.05 (in town) and 1.32 on the boundary with Uzbekistan point first to enrichment of river waters by technogenic uranium on 70% ($\gamma=1$) with the following sorption of this uranium on 60% by riverbed rocks.

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